Interest of molecular functionalization for electrochemical storage

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This review presents the various growing developments of the molecular functionalization in regards to today's electrochemical storage limitations. Fundamental aspects regarding the impacts of the functionalized layers properties on the electrochemical performance as well as perspectives for further developments are also discussed.

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Review Article

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ABSTRACT

Despite great interests of electrochemical energy storage systems for numerous applications, considerable challenges still have to be overcome. Among the approaches to improve the stability, safety, performance and cost of these systems, molecular functionalization has recently been proved an attractive method that allows to tune the material surface reactivity while retaining those of the bulk material. For that purpose, the reduction of aryldiazonium salt is a versatile method that form robust covalent bonds with the material surface with, however, the formation of multilayer structures and (for carbon substrate) sp^3 defects that can be detrimental to the electronic conductivity. Alternatively, non-covalent molecular functionalization based on π-π interactions using aromatic ring units have been proposed. In this review, the various growing developments of the molecular functionalization in regards to today's lithium-ion batteries and electrochemical capacitors limitations is discussed. According to the targeted applications and required properties, both covalent and non-covalent functionalization methods are proved to be very efficient and versatile. Fundamental aspects to achieve better understanding of functionalization reactions as well as molecular layers properties and their impacts regarding the electrochemical performance are also discussed. Finally, concluding perspectives are proposed for future implementation of molecular functionalization in the field of electrochemical storage.

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KEYWORDS
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1. Introduction
Electrochemical energy storage systems are of great interests due to their numerous applications in portable electronics, tools and transportation. However, to fulfill the growing demand for high power and high energy storage devices, considerable challenges still have to be overcome. For instance, despite great advances in materials and electrode engineering [1],[2],[3], the lifetime and safety of the resulted storage devices remain often limiting factors. This originates from the active materials which present relative high reactivity and thermodynamic instability in the real life cycling conditions of electrochemical cells. Depending on the materials and experimental conditions, such instability can lead to various critical phenomena like electrical disconnection and instable SEI in the case of conversion/alloy material [4], severe electrolyte degradation [5],[6] and/or material dissolution [7] at high potentials. Whichever the case may be, most of these phenomena are related to the interfacial reactivity between the electrolyte and the materials of the composite electrode. Therefore, controlling the materials surface properties is of great importance to improve the overall electrochemical performance. To do so, approaches usually rely on a pre-treatment of the materials by surface coating with polymeric [8],[9] or inorganic [10],[11],[12] species and/or on the use of electrolyte additives [13]. Another approach, out of usual paths, based on molecular functionalization has recently been proved an attractive method as it allows to tune the material surface reactivity while retaining those of the bulk material. To achieve this goal, the reduction of aryldiazonium salt is a method of choice due to its versatility and the formation of a robust molecular layer associated with the formation of covalent bonds with the material surface. The later results from a one electron reduction of the diazonium moiety with concomitant formation of an aryl radical. Such functionalization process can be achieved either by electrochemical [14] or spontaneous [15] reduction of the aryldiazonium salts in aqueous [16] and organic [17] media and can be applied to a large variety of substrates such as carbons [17], metals [18] and oxides [19],[20]. One of the most popular industrial applications of this technique is the fabrication of inks and pigments by the Cabot Corporation since 1993 [21]. For more details about reaction mechanisms and chemistry involved with the diazonium functionalization, readers can refer to references [22],[23]. As far as electrochemical storage applications are concerned, it is worth mentioning that: (i) multilayer (oligomer/polymer) structures are systematically obtained [24],[25] unless very strict experimental conditions [26] or specifically designed salts are used [27] and (ii) when carbon serves as substrate, it results in the formation of sp^3 defects which impact the charge transfer and electronic conductivity [28],[29],[30]. Alternatively, molecular functionalization through non-covalent anchoring have recently been proposed in the field of energy storage [31],[32]. It is based on π-π interactions using aromatic ring units such as pyrene derivative for which self-adsorption on sp^2 domains of a carbon surface is thermodynamically driven [33] and results in ideal electrical contacts [33],[34],[35]. So far, the anchoring of pyrene units have been investigated for electroanalysis [36] and sensors [37][38]. Another distinct advantage of pyrene derivatives concerns their redox properties in the sense that their oxidation leads to appearance of redox-active oligomers for which the electrochemistry can be modulated by modification of the functional groups [39],[40].

In this review, the recent developments of the molecular functionalization to address today's limitations of lithium-ion batteries and electrochemical capacitors will be discussed. Literature reports on molecular functionalization for other battery systems are rather scarce and are also discussed in this review. As an overview, Figure 1 described the main strategies implemented so far in the literature. The first part of this review will be devoted to lithium ion batteries and highlights that the molecular functionalization approach has enormous advantages with respect to controlling charge and mass transfer as well as creating artificial interphase. In the second part of this review, the

molecular functionalization will also be shown to play a pivotal role in enhancing pseudo capacitive effects of carbon type electrode materials. Finally, a summary of some fundamental aspects dedicated to achieving better understanding of functionalization reactions as well as molecular layers properties and their impacts in regards to the electrochemical performance will be discussed. Concluding remarks will serve to describe the main perspectives for future implementation of molecular functionalization in the field of electrochemical storage.

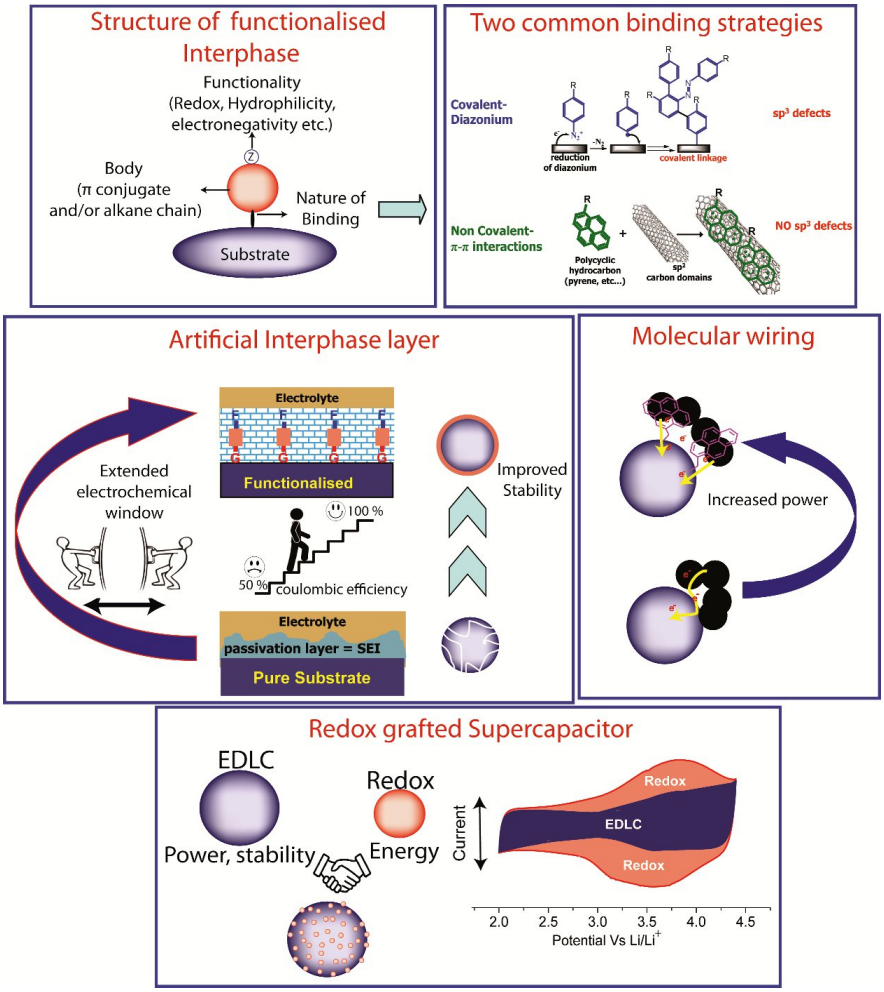

Figure 1 Molecular functionalization strategies for Li-ion batteries and electrochemical capacitors performance enhancement such as artificial interphases, molecular wiring and molecular redox approaches.

2. Lithium ion Batteries application

2.1 Artificial interphases

Among carbon materials for negative electrode of lithium ion batteries, graphite is the most commonly used [41] due to its unique electrochemical properties and low cost. The high performance of the graphite relies, however, on the formation of a stable Solid Electrolyte Interphase (SEI) [42] at its surface during the first lithiation. This aspect is certainly one of the major issue of Li battery because the SEI formation consumes charge irreversibly. Therefore, both the initial irreversible capacity and the ensuing coulombic efficiency on cycling must be optimized. In terms of surface chemistry, the efficiency of the SEI to protect the electrolyte from the graphite without impeding Li intercalation process is therefore of great importance. It is well known that the solvent(s) has a critical role. For instance, the use

of pure propylene carbonate results in the exfoliation of the graphite electrode and the decomposition of the electrolyte [43],[44]. Alternatively, various coatings of the active grains designed prior to the formulation of the electrode have been widely proposed [8],[10]. So far, however, the most commonly used approach to tune the efficiency of the SEI consists in the empirical choice of different electrolyte additives that contribute to and/or structure the SEI [13],[45]. Because these methods rely on relatively weak interactions between the graphite surface and the modified layer (i.e. noncovalent bonding) which can potentially limit the SEI stability, Pan *et al*. [46] have proposed a decade ago to use diazonium chemistry as novel and convenient method to covalently functionalize the surface of natural graphite. The functionalization reaction was performed under nitrogen by stirring natural graphite in a solution of anhydrous acetonitrile containing 4-nitroaniline to which isoamyl nitrite was slowly added to generate the diazonium salt as shown in Figure 2. The resulted modified natural graphite showed higher initial coulombic efficiency as well as better capacity retention for 30 cycles compared to the unmodified graphite (Figure 3). Unfortunately, the coulombic efficiency was not reported in this study.

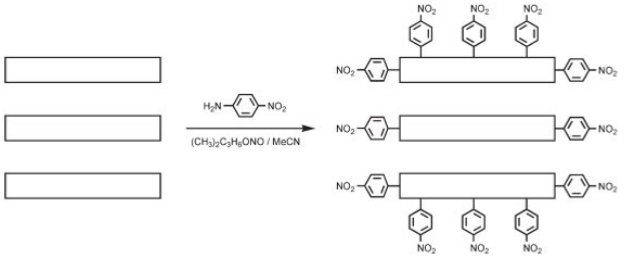

Figure 2 Schematic illustration for the surface modification of natural graphite with 4-nitrophenyl multilayers. Reproduced from Ref. [46] with permission from The Royal Society of Chemistry.

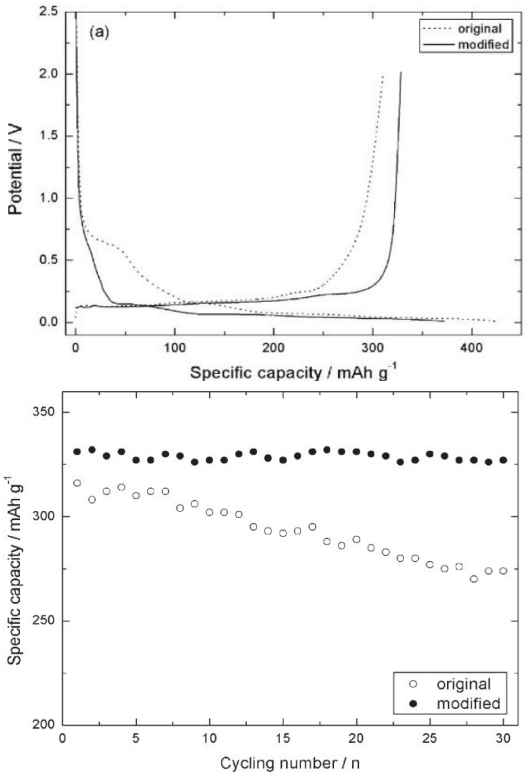

Figure 3 (top) Initial discharge/charge plots and (bottom) the specific capacity as a function of cycling number of the graphite electrodes. Adapted from Ref. [46] with permission from The Royal Society of Chemistry.

More recently, Novák *et al*. [47] explored different functionalization routes using p-carboxylic benzene diazonium salt in aqueous or acetonitrile media which allowed them to tune the loading of the functionalized layer at the graphite surface. They also further modified the functionalized graphite by transformation of the terminal functional group through chemical or electrochemical treatments. This second step resulted in thickening of the functionalized layers. As a whole, they observed that the thicker the functionalized layer was, the lower the extent of the SEI formation was at the expense of a drastic lowering of the reversible capacity. The latter was ascribed to probable insulation of active particles. Exfoliation of the graphite in propylene carbonate based electrolyte was also greatly hindered for high loading. Their results indicate that appropriate functionalization conditions are essential in regards to the resulting and targeted properties for further development.

To replace graphite and increase the energy of

negative electrode in lithium ion batteries, silicon is an attractive material due to its high theoretical specific capacities of about 10 times that of graphite [48]. However, silicon suffers from a massive volume change (>300%) on lithiation and delithiation cycles [48]. It usually results in structural modification, active material pulverization, loss of electrical contact [49] and continuous electrolyte degradation (*i.e*. irreversible charge consumption) due to breaking and re-formation of the SEI during cycling [50]. So far, numerous strategies have been proposed to stabilize silicon-based negative electrodes such as nanosizing, material nano-structuration [51],[52] as well as binders and formulation optimisation [53]. The use of nano-sized Si particles is, however, likely to trigger even more severe electrolyte degradation due to their high surface activity. Molecular functionalization of silicon nanoparticles have therefore been recently investigated as a new strategy to tailor an artificial robust and flexible SEI that would address electrolyte degradation and volume change issues at once. Mazouzi *et al*. [54] used a pH3 buffered carboxymethyl cellulose (CMC) based aqueous slurry to covalently functionalized CMC at the nano-Si particles surface through an esterification reaction between surface SiOH silanol groups of Si particles and COOH groups of CMC. The obtained composite electrode achieves more than 700 cycles at high capacity of 960 mAh g^{-1}, instead of 100 cycles for non-functionalized electrodes prepared at natural pH. Such a drastic cycle life improvement was explained by stronger mechanical contact within the electrode through a networking process of the conductive additive and Si particles during the composite electrode processing. Yang *et al*. [55] showed that Si nanoparticles functionalized by 4-carboxyphenyl groups using diazonium chemistry led to much higher capacity retention upon cycling with about 500 mA h g^{-1} after 50 cycles compared to barely 60 mA h g^{-1} for the bare Si nanoparticles. Li *et al*. [56] showed that varying the surface group of silicon by different surface treatment, including the functionalization of 3-aminopropyltriethoxysilane, led to different electrolyte degradation compounds and electrochemical performance highlighting the key role of controlling the surface functionalities. Abdelhamid *et al*. [57] used thiophene molecules to functionalize Si nanoparticles via an electrochemical process. They showed also that the modified Si retained higher capacity with about 40% of the initial capacity after 60 cycles compared to only 4% capacity retention after 10 cycles for the unmodified Si, more likely due to the formation of an artificial and protecting SEI at the Si nanoparticles surface. Interestingly, they proposed to use such thiophene modified Si nanoparticles as anchor point for further co-polymerization with conducting polymers. Such strategy would allow producing a covalently functionalized Si/conducting polymer anode composite that should in principle mitigate the loss of electrical contact upon cycling.

Another alternative approach based on functionalization through diazonium chemistry has also been recently proposed to stabilize silicon-based electrodes. In order to overcome incomplete and/or non-uniform carbon coating of silicon particles, Du *et al*. [58] covalently functionalized p-phenylenediamine via diazotization onto naturally oxidized surface of Si nanoparticles followed by a carbonizing process at elevated temperature as illustrated in Figure 4. By varying the temperature of the diazotization step, they were able to tune the thickness of the functionalized layer. After carbonization, the resulting Si@C nanocomposite showed significant improvement of the reversible capacity compared to the unmodified silicon (Figure 5).

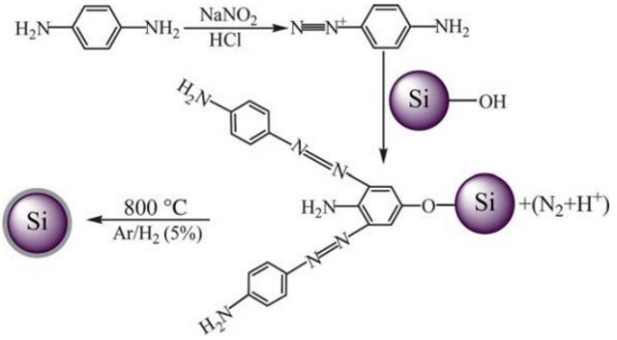

Figure 4 Schematic illustration of the synthesis of Si@C core–shell nanocomposite. Reproduced from Ref. [58] with permission from The Royal Society of Chemistry.

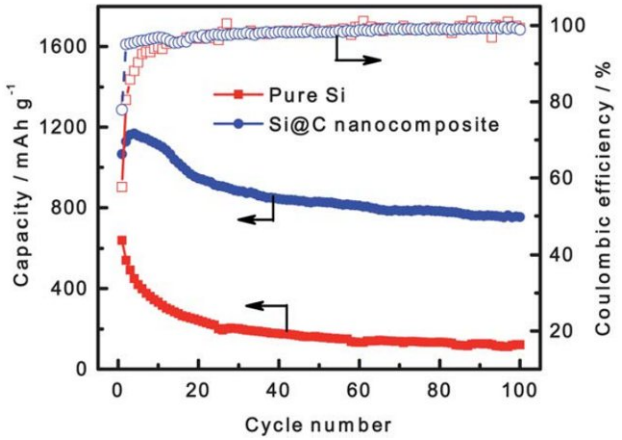

Figure 5 Cycling performance and coulombic efficiency of pure Si and the Si@C core–shell nanocomposite. Reproduced from Ref. [58] with permission from The Royal Society of Chemistry.

More recently, lithium metal has regained interest as negative electrode material through the development of Li-air and Li-sulfur batteries. Despite inherent high energy density and much simpler electrodes processing compared to laminated electrodes, lithium metal still suffer, however, from extensive surface reactivity and poor electrodeposition properties upon cycling. To stabilize lithium metal, various strategies have been proposed including artificial protecting layers and electrolyte optimization [59]. However, impedance growth upon cycling due to SEI film thickening and/or unstable surface morphology still remains a major issue. Alternatively, Marchioni *et al.* [60] then Vaughey *et al*. [61],[62] proposed to use molecular functionalization between the thin native layer of lithium hydroxide of the lithium surface and various chlorosilane derivatives as illustrated in Figure 6. Marchioni *et al*. [60] investigated the possible chemical reactions using multiple techniques and showed that the functionalized silyl derivatives lithium presented a smaller initial interfacial impedance and a lower impedance increase upon immersion in 1M $LiClO_4$ in propylene carbonate. Vaughey *et al.* [61] explained that the enhanced capacity retention of the functionalized silyl derivatives lithium most likely originates from the ability of the functionalized layer to inhibit free solvent attack of the metal electrode surface. By varying the R-group size of various chlorosilane derivatives, they showed that very small R-groups should be preferred to maximize the cycle life [62]. They also showed that pre-cleaning the surface lithium using pentane further enhanced the stability of functionalized silyl derivatives lithium compared to the abrasive cleaning method [62].

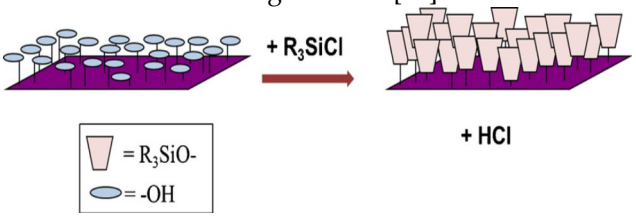

Figure 6 Schematic representation of the silane coating mechanism. Reproduced with permission from Reference xxx. Copyright 2012, Elsevier Ltd.

The interfacial reactivity of positive active materials is also well known to be detrimental to the overall electrochemical stability and performance of lithium ion batteries. For instance, the contact between the active material and the electrolyte may lead to severe electrolyte degradation [5],[6] and/or material dissolution [7], especially at high potential. Similarly to what has been proposed for negative electrodes, common approaches to solve these issues rely on a pre-treatment of the active materials particles by surface coating using polymeric [9] or inorganic [11],[12] species and/or on electrolyte additives [13]. As an alternative, Tanguy *et al.* [63] proposed to lessen the surface reactivity of $Li_{1.1}V_3O_8$ nanograins which show string reactivity toward organic electrolytes more likely due to nucleophilic oxygen sites [64]. The functionalization reaction was performed in situ during Li-ion intercalation using para-nitrophenyl diazonium salt dissolved in the electrolyte. This strategy resulted in a homogeneous organic multilayer film for which the thickness could be modulated depending on the functionalization time as shown in Figure 7. The chemical reactivity of the modified $Li_{1.1}V_3O_8$ toward the electrolyte measured by the extent of the electrolyte decomposition was indeed hindered as deduced from XPS analysis upon cycling. Interestingly, in this conditions, the charge transfer and the electrochemical activity of the modified $Li_{1.1}V_3O_8$ was not impeded when cycled against Li/Li^+. Also, a significant improvement of the capacity retention was observed for the modified $Li_{1.1}V_3O_8$ as shown in Figure 8.

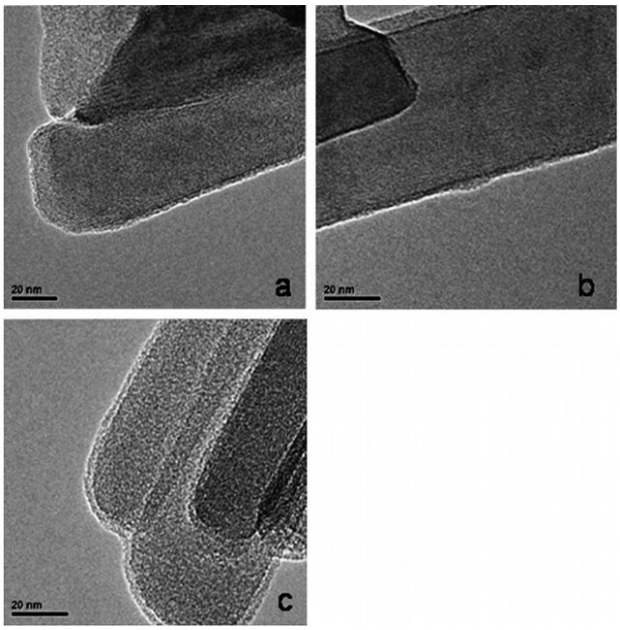

Figure 7 TEM images of (a) modified-$Li_{1.1}V_3O_8$ for 3 min, (b) modified-$Li_{1.1}V_3O_8$ for 10 min and (c) modified-$Li_{1.1}V_3O_8$ for 60. After 3 min, nanograins are indiscernible from those of non-modified-$Li_{1.1}V_3O_8$ while after 10 and 60 min, homogeneous coverage appear at the surface of the modified-$Li_{1.1}V_3O_8$ material of about 1.5 and 2 nm, respectively. Reproduced by permission of The Royal Society of Chemistry.

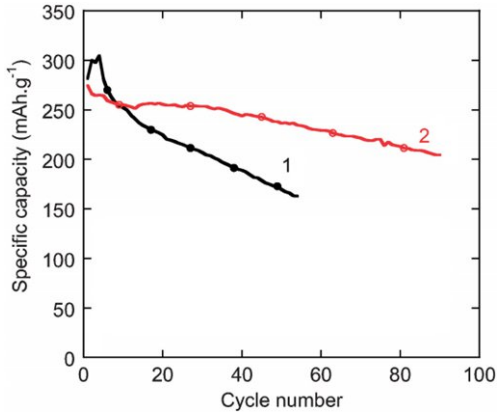

Figure 8 Specific capacity curves for unmodified $Li_{1.1}V_3O_8$ (1) and modified $Li_{1.1}V_3O_8$ (2) as function of cycle number. Adapted by permission of The Royal Society of Chemistry.

Similar improvements of the capacity retention of this material was also achieved using a simple approach that can in theory be readily transferred to industrial processes. The latter consists in self-condensation of phenyl phosphonic acid on $Li_{1.1}V_3O_8$ nanograins in isopropanol [65]. The reaction readily occurs within the suspension and is completed upon approx. 24h.

2.2 Molecular wiring

Electrodes of lithium ion batteries are composite mixtures of redox active material (AM), electron-conducting additives (C) and polymeric binders (B) which architecture (dispersion of AM, C and B, porosity and tortuosity, etc...) greatly influences performance. In particular, regarding today's batteries, it is estimated that 20 to 80% decrease in power performance arises from insufficient electronic conduction [66]. For instance, for carbon coated-$LiFePO_4$ (referred to as LFPC), contact resistance between clusters results in a conductivity drop of more than two orders of magnitude [67]. Another issue regards the mechanical stability of the electrode on lithium insertion/deinsertion which leads to poor capacity retention. This is even more pronounced for negative electrode and most especially for those based on alloy material such as silicon. The design of optimized and stable electronic contact at different scale of the electrode is therefore a key challenge towards cheaper and more efficient batteries. It is not, however, a trivial task because conductive carbon additives are difficult to disperse homogeneously owing to aggregation phenomena occurring within electrode slurries [68]. Moreover, electron transport has been shown to occur through tunneling across adsorbed binders and SEI layers [69] and therefore cannot be controlled during electrode formulation or during cycling. Accordingly, since insulating binders have to be added to the composite electrode, a compromise has to be reached between the electronic conductivity and the mechanical properties of the composite electrode [69]. One of the recent original approach used to tackle these issues consist in connecting ("wiring") AM and C by tethered (covalently or not) molecules or oligomers:

Grätzel's group was actually the first to propose this wiring strategy with use of redox molecular mediators [70] or redox polymers with ''swing" redox active molecules tethered to the polymer backbone [71], to directly wire uncoated $LiFe(Mn)PO_4$ grains to the current collector in order

to improve charge transport. These approaches are based on the electron-hole transport from the redox active molecules to the AM particles. Therefore, the adsorbed molecules should be percolated to allow for cross-surface charge transfer (as is the carbon painting method proposed by Armand *et al.* [72]). Moreover, the redox potential of the molecule should match the Fermi level of active material. Kavan *et al.* [73],[74] implemented this solution by connecting uncoated $LiFePO_4$ to single-wall carbon nanotubes using adsorbed bipyridine complexes. Therefore, these strategies aim at bypassing the use of carbon additives within composite electrodes and do not, however, directly tackle the contemporary concerns of industry-relevant electrodes.

This concern was achieved by Yassin *et al.* [75] who engineered the electronic contacts between the carbon additive and the active material using an extended (≈ 2 nm) thiophene π-conjugated molecular junction. The latter is functionalized by a pyrene unit prone to develop π-π interaction with multiwall carbon nanotube (MWCNT), on one hand, and a phosphonic acid group able to interact with oxides such as uncoated $LiFePO_4$ (LFP) on the other hand (Figure 9, left). This strategy offers the possibility to optimize the electronic transport at the nanoscale which is a key point in enhancing performance of thick electrodes. A vast improvement in the electrode component intermixing was obtained with individual MWCNT being nano-contacted at the surface of LFP grains. Moreover, a much higher electronic conductivity and specific capacity (especially at high C-rates) as well as better capacity retention comparable to that of carbon coated LFP electrodes could be achieved (Figure 9, right) for 2.1 mAh cm^{-2} electrodes. It is worth noting that an adverse effect was, however, observed using the same molecular junctions when replacing uncoated $LiFePO_4$ by the uncoated $Li_4Ti_5O_{12}$ spinel. This serves to show that a charge hopping mechanism may also contribute to the charge transport above 3V vs. Li/Li^+ in addition to tunneling which highlights the crucial role of these molecular junction to carry the flow of the current load at nano-contacts.

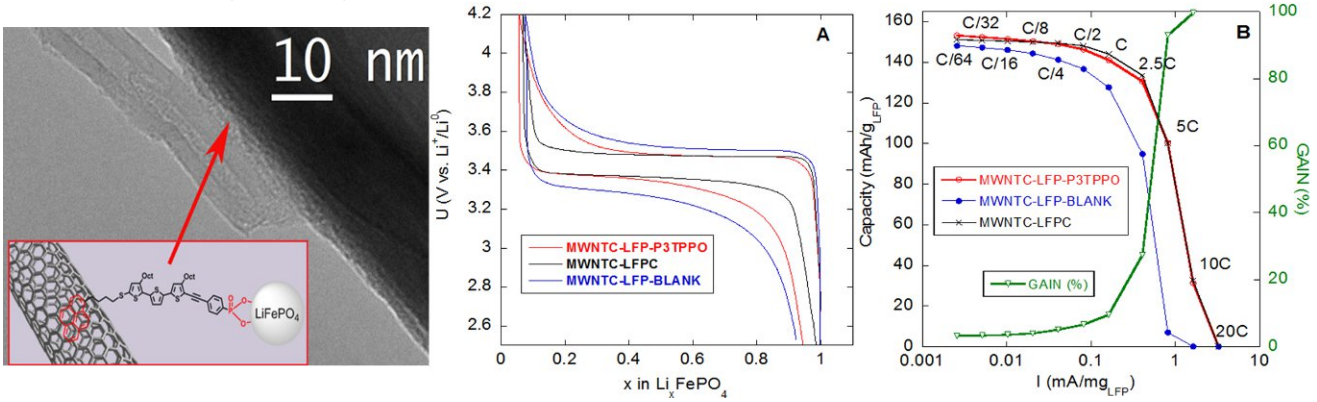

Figure 9 (left) HRTEM image showing an approx. 2 nm molecular junction (marked by an arrow) between carbon nanotube and an uncoated $LiFePO_4$ particle. (right) (A) Charge/discharge profile during the second cycle at C/4 (charge) and C/2 (discharge) rates for carbon coated $LiFePO_4$ hand mixed with MWCNT (black curve), singly grafted (that is to say ''not wired'') uncoated $LiFePO_4$ hand mixed with MWCNT (blue curve) and wired (that is to say ''doubly grafted at both ends of the molecule'') uncoated $LiFePO_4$-MWCNT (red curve); (B) Corresponding power tests along with the capacity gain (green curve). Reprinted with permission from [75]. Copyright 2015 American Chemical Society.

Wiring of C and AM was also achieved in an attempt to decrease the effect of volume changes of AM on cycling [25]. Indeed, chemical coupling of Si nanograins to the carbon additive (graphite [76] and carbon nanotubes [77]) was achieved using several nanometers thick oligo-phenylene derivative. The latter was covalently functionalized at the surface of both materials using diazonium chemistry. This achievement allowed to reach 35 cycles at fixed capacity of 1000 mA h g^{-1} whereas the blank electrode which showed similar coulombic efficiency of 96%, could not reach over 400 mA h g^{-1} [77]. This approach was pursued by Pan *et al.* [78] using graphene sheet as conducting additive. The resulting

nanocomposite delivered a capacity of 1079 and 828 mAh/g in the initial and 50th charge at a current density of 300 mA h g^{-1} with a capacity fading rate of 4.5 mA h g^{-1} per cycle. However, no comparison to a reference electrode was provided in this case.

2.3 Redox molecular functionalization

LIBs have relatively high energy densities (150–250 Wh kg^{-1}) compared to other electrochemical systems due to the faradic reactions that take place within the volume of active grains by simultaneous ion and electron uptake/removal. However, even when fast electronic and ionic motion may occur within the active material, power performance (1–3 kW kg^{-1}) remain frustrated by slow ionic ''refueling'' from the electrolyte because the amplitude of the faradic reactions is large compared to the amount of ions available in the porosity of electrodes [79],[66]. The classical approach for power applications is therefore to make thin electrodes to reduce ionic diffusion path lengths which is, however, detrimental to the energy density of LIBs.

To tackle this issue, Madec *et al*. [80] recently proposed to use surface functionalized anionic redox molecular relay (RMR) for which charge compensation occurs with anions of transference number higher (~0,6) than that of Li cations (~0,2-0.4) in state-of-the-art LIBs organic electrolytes [81],[82]. The interest of RMR is two folds: (i) use the ''dead surface'' of the carbon additive to convey additional faradic capacity and (ii) buffer the drop of Li^+ concentration gradient during high power demand by fast anion mass transport. Therefore, this approach comes to look for any maximum of capacity when screening the mixture of two redox materials: a n type (the active cathode material with Li^+ counter ion) and a p type (the redox molecular layer with anion counter ion). Considering an experimental capacity at 4C rate for LFPC-based electrodes, the authors showed that the maximum capacity gain was estimated to reach up to 80% depending on the surface area, the wt.% content of the functionalized substrates and the surface density (Γ in mol/cm^2) of RMR. Results proved substantial capacity gains as Γ increases. In addition, it was also highlighted that for high RMR loadings, non-covalently functionalized RMR at the carbon additive surface using π-π interactions should be preferred for power applications. Concomitantly, Delaporte *et al*. [83] found that when LFPC was functionalized by lower loadings of organic moieties using the diazonium chemistry, no negative impact was observed on the electrochemical performance.

In order to give a proof of concept, Madec *et al*. [84] functionalized carbon nanotubes (CNT) with a pyrene derivative by simple immersion in a methanol solution (Figure 10). The redox activity of the functionalized CNT originates from the oligopyrene (RMR) formed from pyrene oxidation [39],[40]. Subsequently, electrodes with 10 wt.% of LFPC and 85 wt.% of CNT were used to allow discriminating electrochemical activities of both LFPC and RMR. The resulted cyclic voltammograms (Figure 10) shows the evolution of the relative capacities of unmodified (Blank) and RMR-modified (Hybrid) electrodes. The higher kinetics associated with RMR allowed to obtain a gain higher than 50% at 100 mV s^{-1} (150C rate).

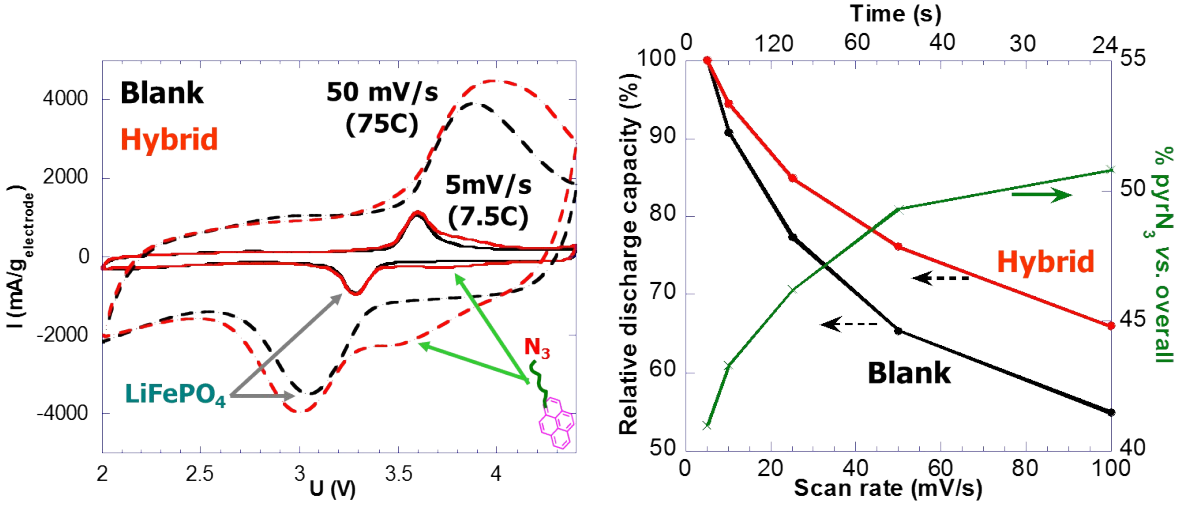

Figure 10 (left) Voltammograms and (right) relative capacities for the unmodified (Blank) and RMR-modified (Hybrid) electrodes made of 10 wt.% LFPC + 85 wt.% CNT (unmodified or RMR-modified) + 5 wt.% PTFE. Adapted from [84].

Redox active organic materials are a possible alternative to today's inorganic insertion materials for Li-ion battery technologies as they usually offer high theoretical capacities, wide accessibility, greener synthesis method and large variety of atoms combination. For instance, in an pioneer study, Poizot *et al*. proposed a new class of organic materials that can be derived from biomass [85],[86]. The main issue of such organic materials is, however, the fast and drastic capacity fading during cycling due to the significant dissolution of the organic materials in the electrolytes commonly used in Li-ion batteries. To overcome this issue, Genorio *et al*. [87] recently proposed functionalized quinone derivative of calix[4]arene (CQ) as organic material at the surface of high surface area nanosized silica and carbon black as insoluble substrates. For the functionalization onto silica, they used a simple condensation reaction between the -COOH groups of the quinone derivative and the surface -OH groups of the silica. To functionalize the carbon black, they first covalently anchored p-aminobenzoic acid using diazonium chemistry then performed a condensation reaction between the -OH groups of the quinone derivative and the -COOH groups of the modified carbon black. As a whole, they observed an improvement of the cycling stability of the organic material compared to the non-functionalized organic material. Pirnat *et al*. [88] then showed that a simple mixture of the quinone derivative and the modified carbon black can lead to close cycling stability compared to the quinone derivative anchored to the carbon black through the condensation reaction. They explained this result by a possible electrochemical reaction between the modified carbon (carbon functionalized with -COOH group) and the quinone derivative. Later, they transferred this organic redox functionalization strategy to graphene nanoribbons (GNRs) using a quinone derivative and again showed improved electrochemical performance compared to the non-functionalized GNRs [89]. At this point, one should note that such molecular organic redox functionalization strategy of high surface area material for battery application remains identical to the redox functionalization strategy proposed earlier and widely developed for electrochemical capacitors application (see following section 3.1).

Another common strategy to stabilize the cyclability of organic-based electrodes for lithium ion batteries is to use redox or radical polymers. The main advantage of such method compared to the molecular organic redox functionalization strategy described previously is the evident increase of electrode capacity that can be obtained due to the decrease of inactive material content in the electrode. However, the use of redox/radical polymers may still lead to the dissolution of the organic material in the electrolyte. Also, the fabrication of well dispersed and electrically connected polymer-based electrodes remains a challenge. Therefore, homogeneous dispersion and strong interaction methods are targeted. In that direction, we should mention the work of different groups that used redox-active nitroxide polymer derivatives covalently functionalized at the carbon nanotubes [90],[91] and reduced graphene oxide surfaces [92] by termination reaction.

2.4 Mass transport, wettability

Lithium metal is envisioned as the ultimate negative electrode for extended driving range of electric vehicles. To do so, dry polymer electrolyte (DPE) which is at the heart of some present-day electrified vehicle batteries [93] have been shown to solve most safety issues encountered with liquid electrolytes. However, the design of more attractive DPEs is hampered by two main concerns: (i) their inability to show both high ionic conductivity and good mechanical property [94] and (ii) the low Li ions transference number t+ (approx. 0.2) [95] which leads to concentration gradient and subsequent dendritic growth [96] especially when considering thick electrodes and/or high rates. Preliminary advances have been made to overcome transport limitations, by the use of polyanionic block copolymers to create a single-ion conductor [97]: the anion is functionalized on one of the blocks such as

these copolymers structurally contain only one mobile charge which is lithium ions. Although such strategy allowed to reach t+ values experimentally close to unity, the low level of ionic dissociation was still restricting conductivities below 5.10^{-6} S cm^{-1} at 60°C. Recently, Bouchet *et al.* [98] solved this issue using a new polyanionic BAB triblock copolymer where the TFSI anion was functionalized on a polystyrene B block associated with a central poly(ethylene oxide) A block (Figure 11). Indeed, the soft $TFSI^-$ anions reduce interactions with Li^+ enabling conductivities half an order of magnitude higher than that of the state-of-the-art values [99] with 1.3 10^{-5} S cm^{-1} at 60°C. Another advantage from tethering TFSI anions is the limited extent of oxidative reactions at the interface (loss of the negative charge [100]) which results in enlarged electrochemical window up to 5V on the positive side. Moreover, this new triblock copolymer presents a tensile stress an order of magnitude higher than that of the blank ABA copolymer without functionalized TFSI which suggests a strong ionic crosslinking between the anionic and PEO domains that would induce self-healing [101]. Finally, owing to the unique combination of these properties, lithium-metal battery prototypes have been demonstrated with an impressive gain in power performances compared with state-of-the-art lithium metal battery technology most especially at 60°C (Figure 11).

Delaporte *et al.* [102] showed using contact angle measurements that a hydrophilic surface was produced after spontaneous grafting of 2.1 wt% of benzene-trifluoromethylsulfonimide groups at the surface of LFPC. Such surface modification which was achieved using aminophenyl and bromophenyl moieties [83] was reported to improve the wettability of the cathode material in organic electrolyte. Electrochemical impedance spectroscopy showed that the resistance of the modified cathode was lowered compared to the bare LFPC electrode. Electrochemical tests for 2.5 mg cm^2 electrodes containing 10 wt.% carbon additive demonstrated that this strategy allows to gain better discharge capacities at C-rate > 2C.

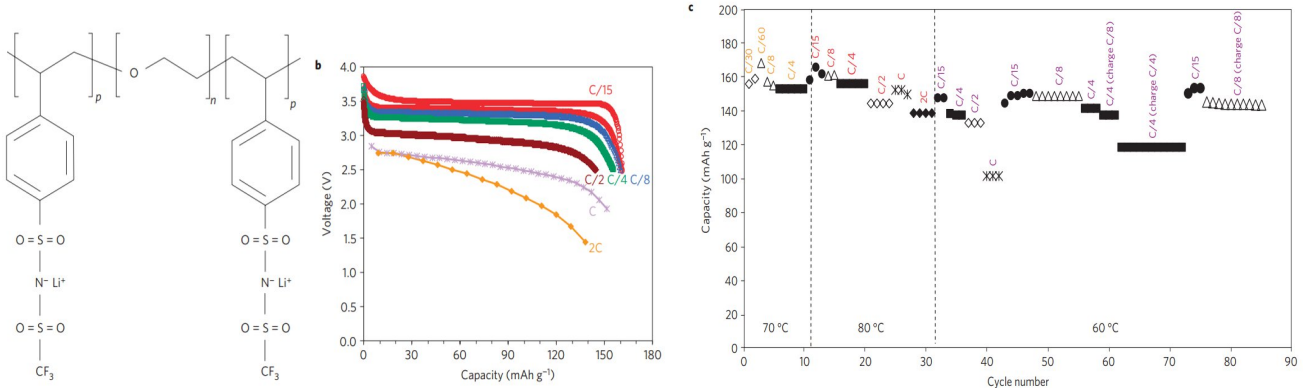

Figure 11 (left) Chemical structure of the new single-ion conductor TFSI_BAB triblock copolymer proposed as an electrolyte for lithium-metal-based batteries. (right) (b) Discharge profiles obtained at 80°C at different rates from C/15 to 2C for a typical prototype Li/TFSI_BAB/$LiFePO_4$ and (c) Cycle-life of the prototype. The different temperatures and C/n rates used are noted in the figure. Reproduced with permission from Reference [98]. Copyright 2013, Nature publishing group.

When dealing with Li-sulfur batteries, the poor capacity retention originates from both the diffusion of soluble polysulfides into the electrolyte and the aggregation of insoluble discharge products (Li_2S_2 and Li_2S) [103]. So far, numerous efforts have been devoted to prevent the loss of soluble polysulfides using encapsulating carbon matrix, wrapping with polymers, graphene and metal oxide or adding an interlayer between the cathode and separator [103]. To deal with the sequestering aggregation of insoluble discharge products, amphiphilic polymers have been showed to enhance the binding energy between the insoluble discharge products and the carbon matrix which resulted in improved capacity retention upon cycling [104]. However, the bulky nature of the used amphiphilic polymer can lead to

inhomogeneous functionalization and ineffective sulfur infiltration by pore blockage. To overcome this issue, Kim *et al*. [105] functionalized commercial ordered mesoporous carbon (CMK) by p-phenylenediamine using the diazonium chemistry. The resulted aniline functionalized CMK showed improved capacity retention and coulombic efficiency over 50 cycles at 0.1C rate compared to the unmodified CMK. This improvement was attributed to the moderate diazotation condition that maintained the original microstructure of the CMK while homogeneously functionalized aniline groups that provide strong Lewis acid-base interaction to immobilize insoluble discharge products.

3 Electrochemical capacitors application

3.1 Redox molecular functionalization

Electrochemical capacitors are known for high power densities (10 kW kg^{-1}) and extremely long cycle life owing to fast surface charge storage through capacitive ion adsorption and pseudocapacitive surface redox reactions [106],[107]. As a result, they are, however, plagued with low energy density (5 Wh kg^{-1}). To improve the capacity/energy of electrochemical carbon based capacitors, surface functionalization of redox active molecules is one of the two main strategies, the other one consisting in the control of the pore size [107]. According to this approach, the gravimetric capacity, the potential and the wt.% of the redox molecules governs the additional energy that can be expected while the impact of the functionalization on the porosity and sp^2 domains define the power properties of the resulting material. Lastly, the stability of the molecule anchoring at the surface of the carbon material together with the reversibility of the faradic reactions are also key parameters that need to be taken into account.

In 2004, Leitner *et al*. [108] were the first to propose carbon surface functionalization by redox molecules through simple adsorption of 2-nitro-1-naphthol on carbon electrodes followed by the electrochemical formation of quinone groups which can then be reversibly reduced to hydroquinones. In 0.5 M H_2SO_4, this resulted in an enhancement of the capacitance from 65 F/g to 250 F g^{-1} in a 0-0.5 V potential window vs. SCE. However, the low working potential of the redox couple made such functionalized electrodes less attractive for the application. Furthermore, the weak interaction of the physically adsorbed molecules rises some doubts about retention of the additional capacity upon cycling. Accordingly, since this pioneer study, stronger molecules/substrate interactions via both covalent and non-covalent functionalizations have been developed.

Covalent approach – In 2008, Kalinathan *et al*. [109] were the first to use of diazonium to covalently anchored anthraquinone (AQ) group at the surface of carbon fibers. The capacitance of the electrode was increased form 1.15 F to 1.62 F in 0.5 M H_2SO_4 between -0.3 V and 0.6 V *vs*. Ag/AgCl with only ~7 wt.% molecule loading. Based on this study, Algharaibeh *et al*. [110] reported the first asymmetric electrochemical capacitor cell using an AQ functionalized carbon as negative electrode and RuO_2 as positive electrode with a 1.2 V potential window. Later, they also proposed the first asymmetric electrochemical capacitor cell based on positive and negative carbon electrodes functionalized by dihydroxybenzene and anthraquinone groups, respectively [111]. This approach allowed a twofold increase of the cell energy. Lebègue *et al*. [112] also demonstrated a promising asymmetric electrochemical capacitor based on 2,2,6,6-tetramethylpiperidine-N-oxyl and naphthalimide as functionalized redox molecules at the positive and negative carbon electrodes surface, respectively (Figure 12). Compared to AQ, naphthalimide allows lowering the working potential of the negative electrode. The capacitance of the full cell was also doubled. Very interestingly, the anodic decomposition of the electrolyte was lowered after functionalization which allowed to increase the voltage cell window from 1.9 V to 2.9 V.

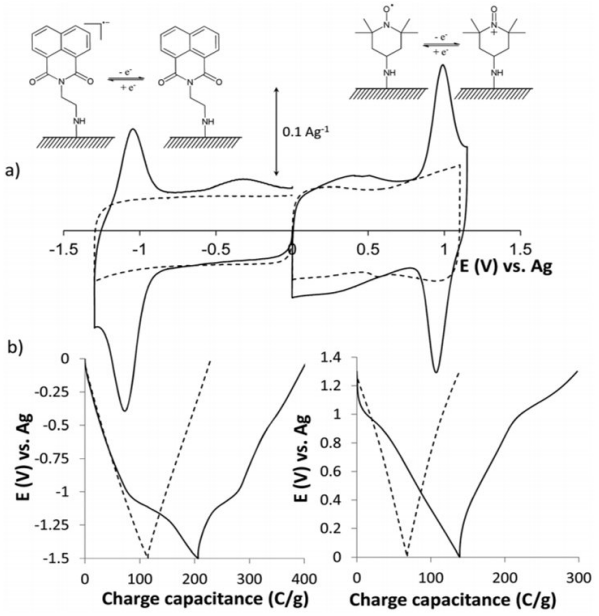

Figure 12 (a) Cyclic voltammograms of the TEMPO-modified positive carbon electrode and the naphthalimide-modified negative carbon electrode recorded in propylene carbonate (PC) + 1 M Bu_4NBF_4 at a scan rate of 1 mV s^{-1} (~3C rate). (b) Galvanostatic charge–discharge curves of the naphthalimide–AC composite (on the left) and the TEMPO–AC composite (on the right) at a current of 0.1 mA. Reproduced by permission of The Royal Society of Chemistry.

Anthraquinone (AQ) is probably the most extensively studied redox molecules for functionalization [113],[114]. Investigation of the electrochemical response of AQ functionalized carbons revealed that the redox potential linearly decreases with the electrolyte pH with, however, a constant 2 electron redox process throughout the pH range [115]. Therefore, the redox potential of AQ is ideal in alkaline media for negative electrode with -0.8 V *vs*. Ag/AgCl. However, at pH 14, AQ forms a dianion that produces a repulsive interaction with negatively charged electrode surface. This process results in the departure of molecules that remain adsorbed at the carbon surface during the uncomplete covalent functionalization reaction through the diazonium chemistry. To avoid this phenomena, a modified electrochemical functionalization process of AQ was proposed to increase the stability in alkali medium as discussed later [116]. Interestingly, an analogue molecule of AQ, 9,10-phenanthrenequinone (PQ) showed superior stability upon cycling at the expense of a 300 mV positive redox voltage shift [117],[118]. This higher stability was explained by a more efficient covalent functionalization along with the presence of the two ketone groups on the same side of the PQ molecules which makes PQ more hydrophobic than AQ, thus greatly hindering any possible desorption/dissolution from the carbon surface. Le Comte *et al*. [119] then took advantage of PQ to prepare hybrid electrochemical capacitors coupling PQ-functionalized carbon and $Ni(OH)_2$ as negative and positive electrodes, respectively.

Recently, an interesting approach was proposed by Legoupy *et al*. [120] to significantly increase the number of electrons exchanged per functionalized molecules. To do so, they combine a rhodizonic acid with a benzenediamine through simple condensation and further functionalization of the obtained multi-electron redox active molecule at an activated carbon surface using the diazonium chemistry (Figure 13). The resulted functionalized molecule could exchange 3.6 electrons thus greatly increasing the capacitance by a 3.5 factor compared to the unmodified carbon electrode.

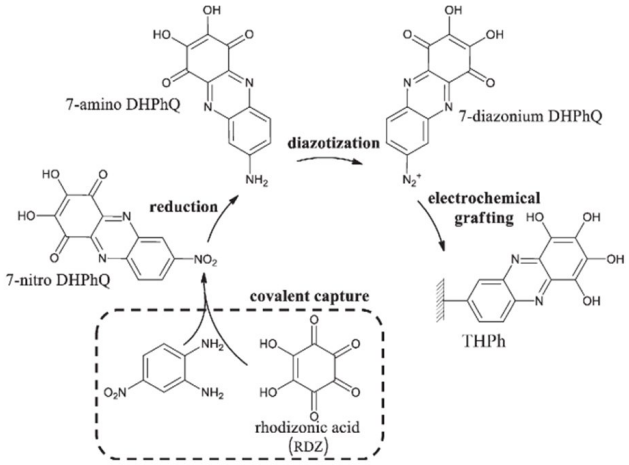

Figure 13 Schematic illustration for the grafting of an oxocarbon compound. Reproduced with permission from Reference [120]. Copyright 2016, Elsevier Ltd.

In a totally different approach, Benoit *et al*. [121] used the possibility of functionalizing a catechol redox derivatives onto a polystyrene polymer binder rather than on a classical carbon surface (Figure 14). This strategy allowed to avoid the decrease of the double layer capacitance and the resulted ionic

transport hindering that arises from the disturbance of pores when carbon are functionalized.

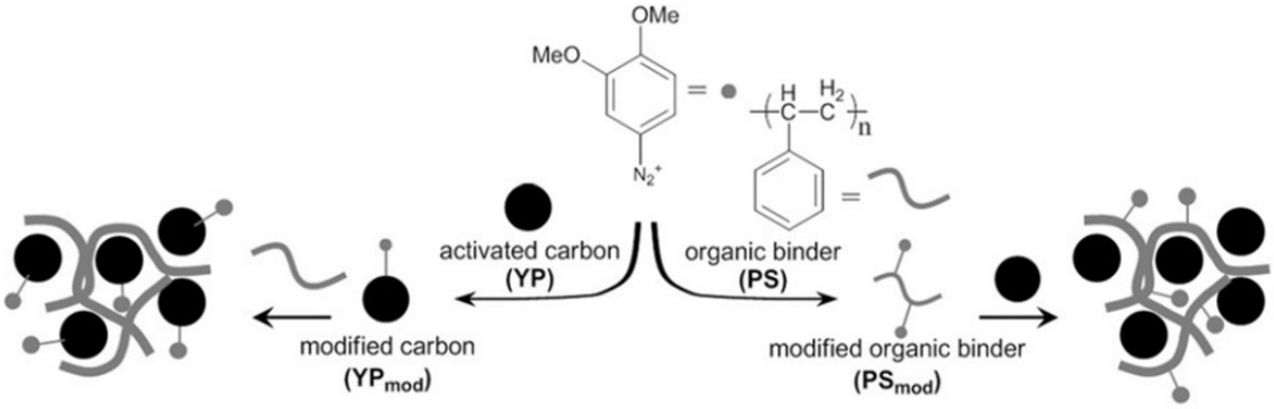

Figure 14 The two different routes used for introducing electroactive molecules on the electrode materials. Adapted from reference [121] with permission of Wiley.

Non-covalent approach – While non-covalent interaction may be seen as too weak for application that requires thousands of cycles, the stability of the system can be efficiently enhanced by using π-π interactions. In this case, several advantages over covalent functionalization result: (i) they are thermodynamically driven [33] so in principle they do not require any complex functionalization procedure and (ii) they do not significantly alter electrical contacts [33],[34],[35] Madec *et al.* [31] recently reported the use of strong π-π interaction between graphitised carbon fibers (CFs) electrodes and a pyrene derivative (Figure 15). The selected multi redox pyrene was simply added as an additive in standard LP-30 electrolyte and self-adsorbed by π-stacking interactions either during OCV or cycling of the cell. Depending on the potential window, the adsorbed pyrene units can further oligomerize at the surface of the carbon which further secure their immobilization. This strategy resulted in an increase of the capacity from 13 mAh $g_{substrate}^{-1}$ (19 F $g_{substrate}^{-1}$) for the bare electrode to 36 mAh $g_{substrate}^{-1}$ at 100 mV s^{-1} (150C rate) between 2.0 and 4.4 V *vs.* Li/Li^+ with an excellent stability over 60000 cycles (Figure 15).

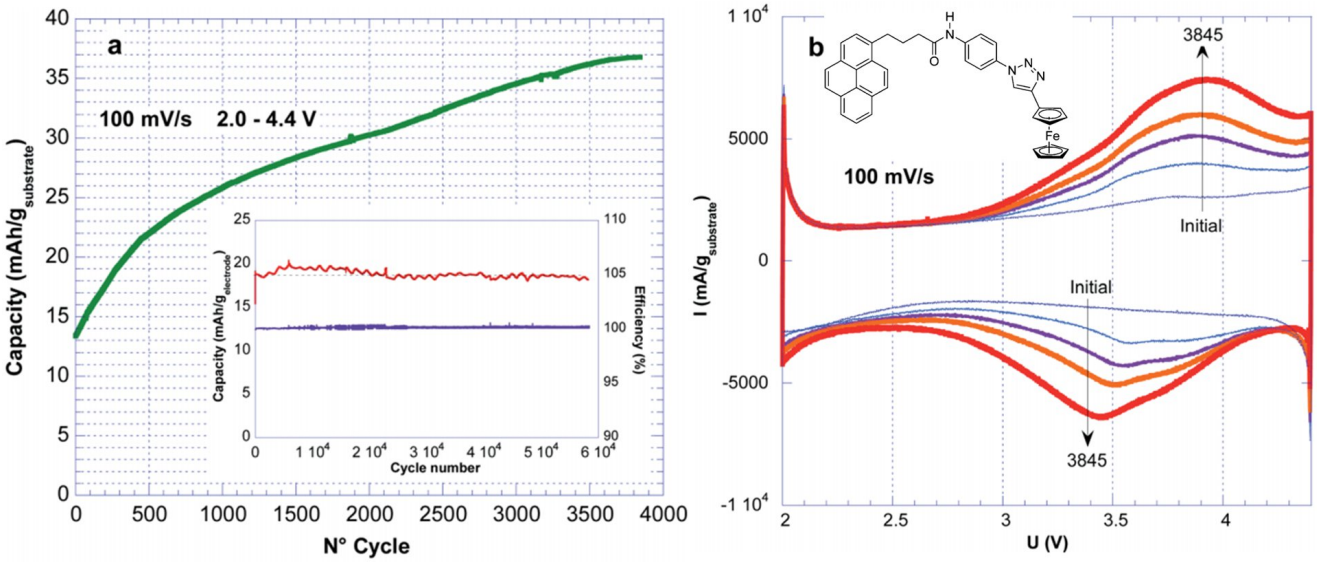

Figure 15 (a) Evolution of the capacity during cycling of a CF composite electrode in electrolyte containing the multi redox pyrene derivative (MM) as additive at 100 mV s^{-1} (150C rate) within 2.0–4.4 V and (b) corresponding voltammograms. Inset: cycle life of a CF-MM electrode obtained upon immersion in MM-electrolyte for 10 days. Oscillations correspond to periods of 12 h and are therefore associated with day/night

temperature variations. Adapted by permission of The Royal Society of Chemistry.

Later, Bachman *et al*. [122] followed this approach by comparing three different pyrene derivatives (pyrene, 1-amino-pyrene and 1-pyrenecarboxylic acid). They showed that oxidized few-walled carbon nanotubes (FWNT) functionalized by 1-amino-pyrene achieved the highest capacity (175 mAh $g_{electrode}^{-1}$ (210 F $g_{electrode}^{-1}$) between 1.5 and 4.5 V *vs*. Li/Li^+ in 1M $LiPF_6$ EC:DMC (3:7 by volume)) compared to the other pyrene derivatives presumably due to electrostatic interaction between the oxygen functional groups of the oxidized FWNT and the protonated amino groups of the pyrene. Borenstein *et al*. [123] also took advantage of non-covalent π-π interactions by using 1,10-phenanthroline as an additive to functionalize the surface of an activated carbon. Thanks to the two redox processes of the phenantroline, the capacitance of the electrode was increased from 110 F $g_{electrode}^{-1}$ for the bare electrode to 190 F $g_{electrode}^{-1}$ in PC-based electrolyte. No adverse effect of the functionalization was observed on the power capability and capacity retention upon 8000 cycles. Interestingly, the addition of phenanthroline allowed increasing the electrochemical window from 3 V to 3.4 V presumably due to remaining phenantroline molecules in the electrolyte that are charged and therefore increase the charge carriers' concentration as deduced from EIS experiments. Authors also claim that dissolved phenanthroline behave as redox shuttle. An *et al*. [124] immobilized anthraquinone on graphene and increased the capacity by two with a final capacitance of 400 F g^{-1}. They also proposed an asymmetric electrochemical capacitor using the functionalized graphene electrode as negative electrode and graphene as positive electrode in aqueous H_2SO_4 electrolyte which presents, however, a restricting cell voltage of 1 V. The same group [125] then reported the functionalization of alizarin on graphene aerogel. Alizarin showed two reversible redox couples from the hydroxyl and carbonyl groups and the resulted composite electrode showed greatly enhanced capacitance with 350 F g^{-1} compared to 31 F g^{-1} and 162 F g^{-1} for the alizarin and the unmodified graphene aerogel, respectively.

As a whole, the functionalization of redox molecules have been proven to be a very powerful and efficient strategy to enhance the energy density of electrochemical capacitors. The effect of the functionalization on the pore structure as well as the control of the molecular coverage and its stability during cycling are, however, critical point in regards to the power density.

3.2 Other purposes

Wiring – The approach of wiring between the active material and the carbon additive through a molecular junction (Lithium ion Batteries application, section 2.2) was recently extended to electrochemical capacitors by Ramirez-Castro *et al*. [126]. They used the diazonium chemistry to first chemically functionalized the carbon black particles then connect amorphous manganese oxide (MnO_2) particles. The capacitance of the resulting MnO_2-carbon nanocomposite electrode was doubled compared to a simple mixture of the two components and also retained at faster cycling rates, thus highlighting the role of intimate coupling of MnO_2 and carbon.

Wettability – In carbon-based electrochemical capacitor, the charge storage mechanism is based on the charge separation at the solid/liquid interface between the carbon and the electrolyte. In a simple case, during charge, anions/cations from the electrolyte compensate the positive/negative charge at the positive/negative carbon electrodes, respectively. Such mechanism leads, however, to a depletion of ions in the bulk electrolyte during charge due to the formation of the electrical double layer at the electrolyte/electrode interfaces which results in a significant decrease of the ionic conductivity of the electrolyte. To tackle this issue, it is possible to decrease the thickness of electrolyte between the two electrodes, having in mind that the amount of ions should remain sufficient to allow a full charge of the electrodes. In that direction, Pech *et al*. [127] functionalized a high-surface area carbon by phenylsulfonate groups using the diazonium chemistry to control the conductivity gradient within the electrolyte (Figure 16). They showed by in situ measurements of the electrolyte resistance of a two electrodes electrochemical capacitor that the

functionalized anionic species can avoid ionic depletion upon charging, therefore maintaining a high level of conductivity (Figure 16). One can also note that the functionalization of hydrophobic (-CF_3) or hydrophilic (-SO_3H) functional groups have also been proposed to control the wettability of carbon by the Cabot corporation for inks fabrication for instance [128],[129].

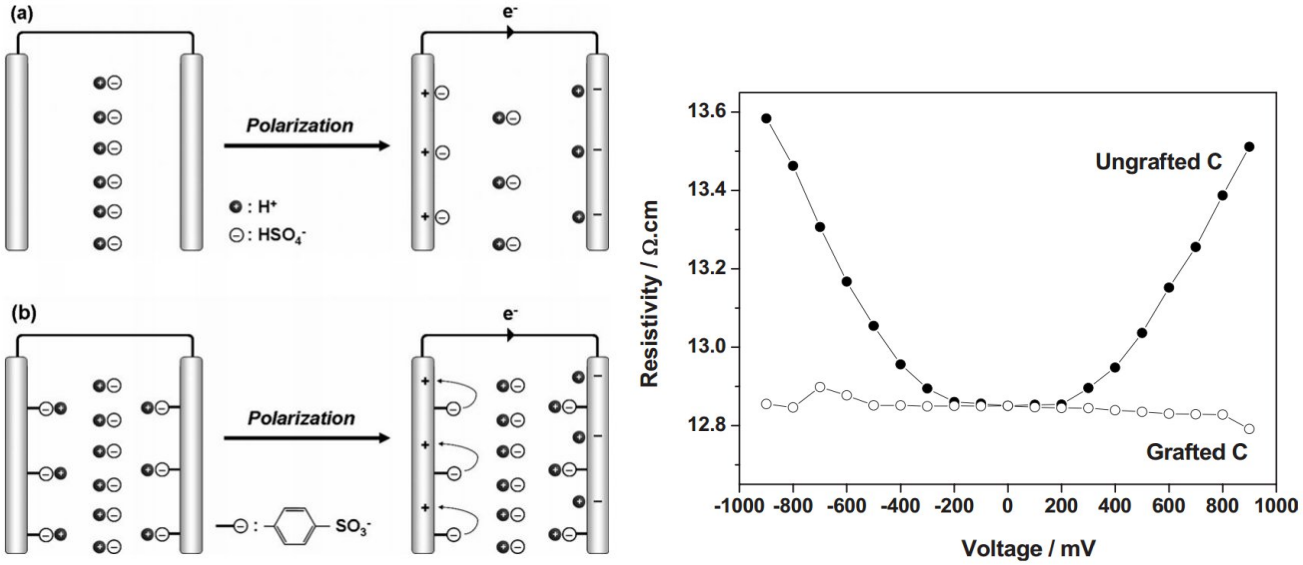

Figure 16 (left) Schematic representation of the mechanism occurring on carbon electrodes polarized in H_2SO_4 media: (a) unmodified carbon electrodes and (b) carbon electrodes modified with sulfophenyl groups. (right) Plot of the resistivity of the 0.1 M H_2SO_4 electrolyte in a two electrodes symmetrical capacitor as a function of the applied potential. Reproduced by permission of The Electrochemical Society.

Binder formulation – To prepared electrochemical capacitor and battery composite electrodes, electro-active material, conductive carbon additive and binder are usually mixed together to form a paste/slurry that is eventually tape cast to obtain an electrode film. It is well known that both binder and formulation properties have strong impacts on the electrochemical performance. In that direction, Assresahegn *et al*. [130] recently proposed to covalently functionalized a polyacrylic acid (PAA) layer with "binder"-like properties at the surface of a highly porous carbon in order to prepare a material with both charge storage and binder properties for electrochemical double-layer capacitor (Figure 17). The modified carbon was prepared via a two-step process consisting in the covalent anchoring of a thin polymerization initiator layer using the diazonium chemistry followed by the further polymerization of PAA using atom transfer radical procedure. The resulted modified carbon used in composite electrodes was found to be more hydrophilic which resulted in better wettability in an aqueous electrolyte compared to the unmodified carbon. Much higher specific capacitance and capacitance retention upon cycling (99.9% after 5000 cycles) was also observed for the modified carbon in an aqueous 0.65M K_2SO_4 electrolyte compared to the unmodified carbon as well as a wider working potential window. They proposed that the improved performance can be explained by ionizable carboxylate surface groups that can allow good electrolyte accessibility to the pores, surface wettability of the active layer, high ionic conductivity and good chemical and mechanical stability in aqueous electrolyte.

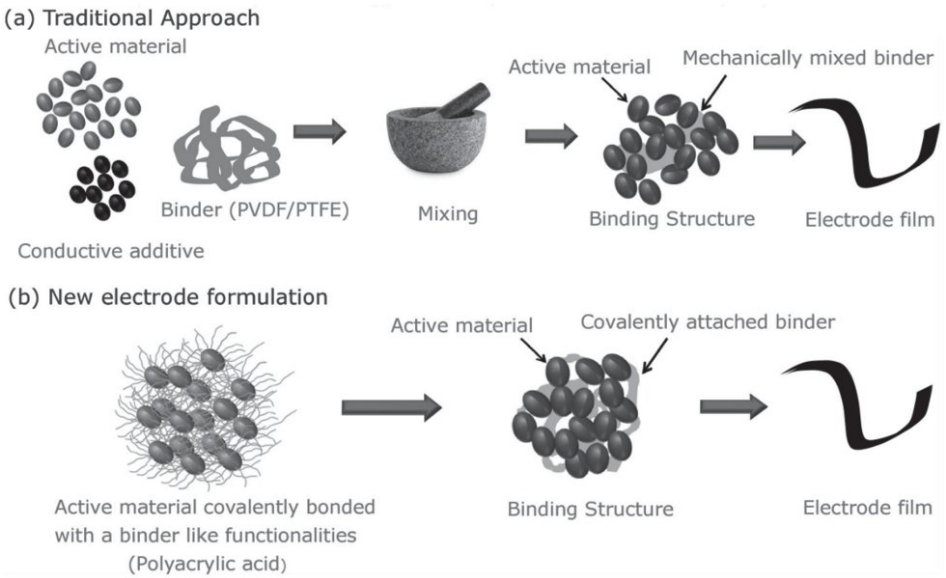

Figure 17 Schematic representation of the: a) traditional approach for the fabrication of a composite electrode and b) the new electrode formulation based on bifunctional materials. Reproduced from reference [130] with permission of Wiley.

4. Fundamental aspects

In this section, studies dedicated to the understanding of the functionalized layers properties and their impacts in regards to the electrochemical performance will be discussed.

4.1. Control and stability of the functionalized layer

O*ptimisation of the molecular coverage* – Fundamental understanding of the diazonium reduction mechanism as well as determination of optimal experimental conditions has been widely studied and are crucial from the application viewpoint as the main characteristics of the modified substrate relate to the extent and homogeneity of the molecular coverage. For instance, some studies are dedicated to the development of more reliable technique to estimate the functionalization loading [131] such as using quinone derivatives with an halogen atom as internal probe [132],[133]. Also, the spontaneous functionalization of carbon powders is very convenient but results, however, in relatively low functionalization loading [134]. As a result, many groups have been intensively searching for new ways to increase the molecular coverage (*i.e.* functionalization loading) [131],[134] especially for electrochemical storage applications. In particular, Lebègue *et al*. [135],[136] showed that when carbon surfaces are functionalized by spontaneous reduction of diazonium salts generated *in situ* in water media, the use of an organic acid substituent instead of an external acid source greatly improved the functionalization loading. As an alternative approach, Madec *et al*. [137] recently achieved extremely high functionalization loadings of p-nitrobenzene diazonium salt at the surface of the carbon coated $LiFePO_4$ core shell material. Electrochemical, XRD and EELS experiments proved that the oxidation of the $LiFePO_4$ core delivers large amounts of electrons to the carbon shell at a constant energy above the Fermi level of the diazonium salt. Results showed, however, a much higher functionalization loading for LFPC than the sum of those measured for carbon coated $FePO_4$ and bare $LiFePO_4$, therefore highlighting a synergistic effect (Figure 18). The latter was ascribed to the carbon shell that appeared mandatory to trigger a highly effective reaction. This synergy allowed unprecedentedly up to 10 times higher loadings compared to those usually obtained for such spontaneous functionalization at the surface of amorphous carbon [24]. Interestingly, close examination of the grafted grain agglomerates by EFTEM EELS mapping revealed that functionalized and oxidized core-shell grains are not spatially correlated (Figure 18).

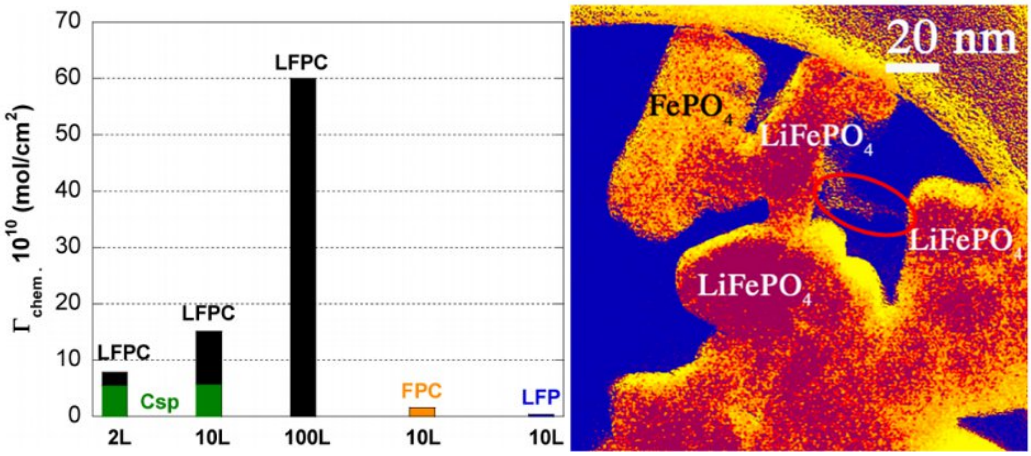

Figure 18 (left) Comparison of the functionalization loading (Γ_{chem}) showing the synergistic effect of the carbon coated $LiFePO_4$ core-shell (LFPC) with different amount of PNBDiaz (nL) compared to the carbon coated $FePO_4$ shell only (FPC) and uncoated $LiFePO_4$ core only (LFP). (right) EFTEM EELS mapping image of the functionalized LFPC-10L. Purple crystals correspond to a phase of composition close to $LiFePO_4$ while orange ones correspond to a phase of composition close to $FePO_4$. Edges of crystals sometimes appear orange due to extreme surface plasmon effects, as well as at the carbon coating. Reprinted with permission from [137]. Copyright 2013 American Chemical Society.

Anothumakkool *et al*. [138] recently reported a simple strategy that consists in the polymerisation of π-stacked 1-nitropyrenes on carbon onion (OLC) using an initial in-situ electroreduction of the -NO_2 groups. The reduction of -NO_2 to -NH_2 decreased the oxidative polymerization potential of the pyrene units which eventually increased the functionalization loading in comparison with pyrene derivatives without nitro groups. Density functional theory (DFT) calculations and experimental results showed that graphitised OLC have strong interaction with pyrene containing an electron acceptor group (-NO_2) compared to electron donor group (-NH_2), in agreement with the report of Bachman *et al*. [122]. Following this strategy, functionalization loading of ~20 wt.% was reached and the resulted 1-nitropyrene functionalized OLC showed a capacity of 45 mAh g^{-1} compared to 20 mAh g^{-1} for the unmodified carbon.

Stability of the functionalized layer – When carbon electrodes of electrochemical capacitors are functionalized with redox molecules using the diazonium chemistry, a continuous decrease of the faradic capacity during cycling is often observed. Depending on the efficiency of the diazotation reaction, part of the reactants are only physisorbed at the carbon grains surface or even embedded in the resulting oligomers. Accordingly, the capacity loss during cycling was mainly ascribed to desorption of the molecules. Pognon *et al*. [114] showed that while higher loading improved the capacitance, the fraction of adsorbed molecules was increased which resulted in higher capacity loss especially during initial cycles. This was further confirmed by Le Comte *et al*. [117] that thoroughly compared adsorbed and covalently functionalized carbon black Pearls electrodes by 9,10-phenanthrenequinone. They showed that only the covalently functionalized 9,10-phenanthrenequinone led to stable capacity during cycling. To tackle this issue, Le Comte *et al*. [116] improved the capacity retention issues by triggering the diazotization/functionalization reaction either chemically using sodium nitrite or electrochemically after formulation of the composite electrode (Figure 19). The resulting functionalized carbon-based electrodes showed slightly higher stability upon cycling in aqueous 1 M KOH. Interestingly, this new procedure also allowed to save significant time and solvents which are also important parameters from the application point of view. Another approach to deal with the desorption of molecules is to restrict the functionalization reaction of diazonium salts to a molecular monolayer

as recently proposed by Menanteau *et al*. [139],[140]. To do so, they used a radical scavenger in solution which led to low molecular mass fraction and improved electrochemical stability upon cycling. Note that when radical scavenger was used, more facile mass transport was observed due to diminished clogging effect of the pore structure [140]. This latter point, known to be critical, is discussed later.

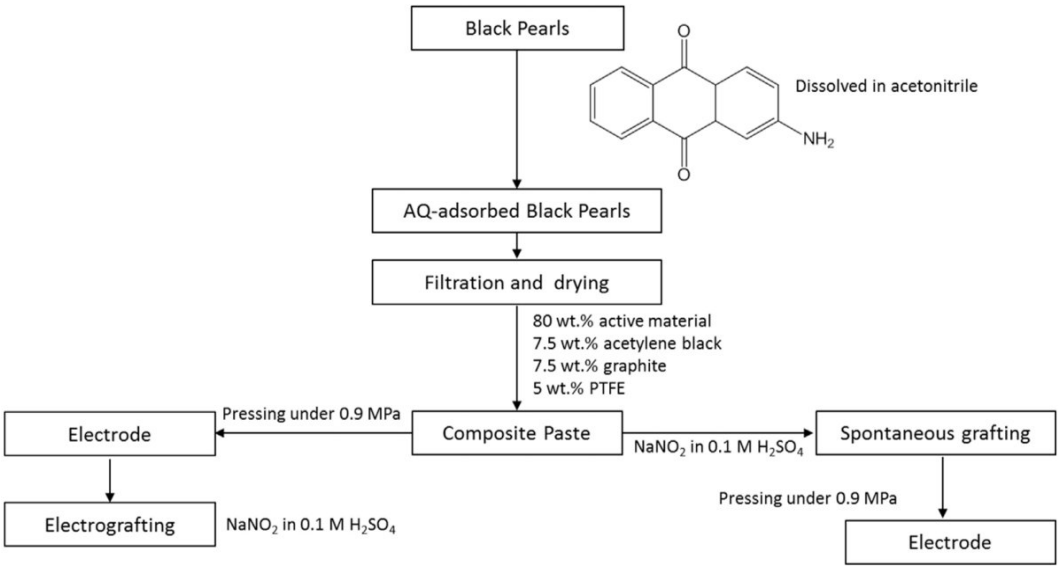

Figure 19 Flowchart for the grafting processes. Reproduced with permission from Reference [116]. Copyright 2014, Elsevier Ltd.

4.2 Impact of the functionalization on the electrochemical properties

Charge transport - While it is well known that the electron transport in carbon substrate functionalized by the diazonium chemistry is impacted due to the formation of sp^3 defects [28],[29],[30],[80] little is known, however, about the electron transport within the functionalized molecular layer. Towards this objective, Madec *et al*. [84],[141] recently investigated the charge transport mechanisms of carbon coated $LiFePO_4$ (LFPC) functionalized by 4-ethynylbenzene (EB) diazonium salt using broad band dielectric spectroscopy (BDS). The choice of LFPC was motivated by the occurrence of a thin carbon coating for which the electron properties should in principle be more sensitive to surface functionalization. As expected, results confirmed that the functionalization of LFPC significantly impedes the kinetics of Li intercalation (Figure 20). Interestingly, authors noticed that simple immersion in the polar solvents used for the functionalization process also resulted in hindered intercalation kinetics (Figure 20). Due to their high dipole moment, strongly physisorbed molecules that were detected by XPS likely added barriers to electron hopping. Indeed, electronic conductivities of LFPC samples significantly decreased upon simple immersion in these polar solvents and decreased even further after covalent functionalization (Figure 20). Broadband dielectric spectroscopy (BDS) showed that after covalent functionalization, long range electron transport through the carbon coating was no longer possible due to higher sp^3 content as proved by Raman spectroscopy. However, the electron transport appeared to be redirected through functionalized oligomers for which relatively low activation energy allowed higher conductivity at low temperature (T <250 K).

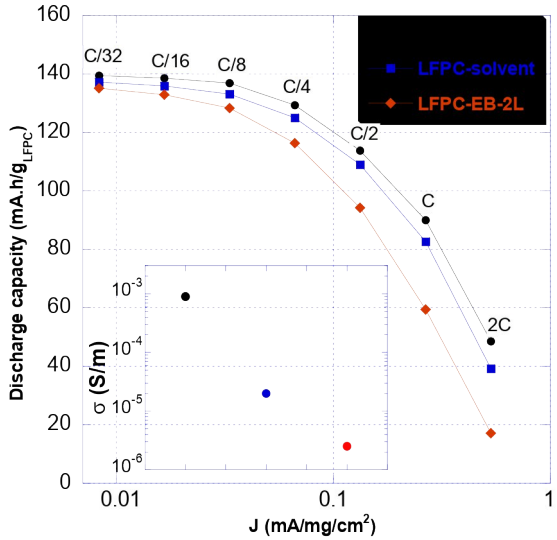

Figure 20 Signature curves for unmodified LFPC (blank), LFPC-solvent and LFPC-EB. Adapted from [84]. Inset: Conductivity for unmodified LFPC (blank), LFPC-solvent and LFPC-EB at room temperature as measured from Broadband dielectric spectroscopy. Adapted from [84].

As previously discussed in section 2.3, similar detrimental effect on the intercalation kinetics of LFPC was also observed when the conductive carbons black of LFPC-based electrodes was covalently functionalized by the diazonium chemistry. To overcome such limitation, Madec *et al.* [80] showed that the use of non-covalent functionalization via π-π interactions using a pyrene derivative did not impede the intercalation kinetics of LFPC. Therefore, for power applications, pyrene derivatives appears as a promising alternative.

Ionic transport - When porous materials such as carbons for electrochemical capacitors are functionalized, one have to consider the impact of the functionalization on the porous network as it may decrease electrolyte accessibility. Indeed, Toupin *et al.* [134] first showed that depending on the synthesis conditions, the diazonium chemistry resulted in a decrease of the microporosity due to the presence of the functionalized moieties at the entrance of the micropore. Pognon *et al.* [114],[142] also showed that activated carbon (~1500 m^2 g^{-1}) functionalized by different loadings of anthraquinone (AQ) derivatives via the diazonium chemistry led to a large decrease of the microporosity and a concomitant loss of the BET surface area even for small loadings (Figure 21, 22). When loading were as high as 7 wt.%, both microporosity and mesoporosity were strongly impacted. Interestingly, despite a detrimental effect of the functionalization on the microporosity and BET surface area of the activated carbon, the double layer capacitance was only slightly affected (Figures 20, 21). Authors observed that while more than two times lower microporous and BET surface areas was measured with a 14 wt.% loading, the double layer capacitance was only decreased by ~15%.

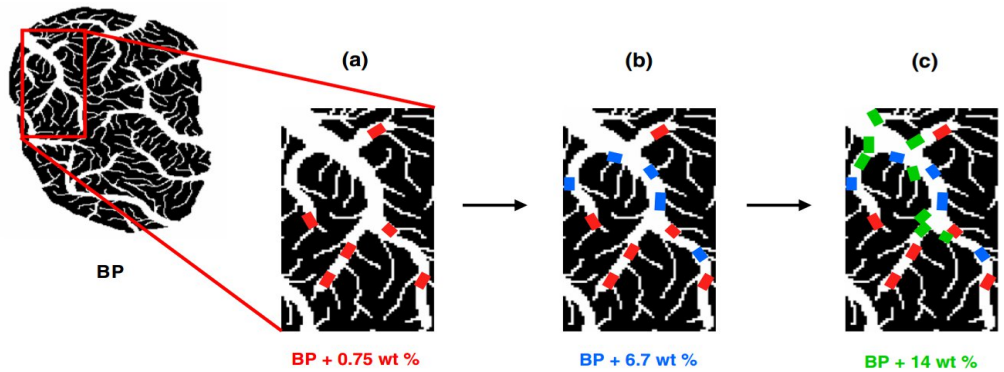

Figure 21 Schematic representation of how the porosity is affected by the grafting of AQ molecules: smaller pore entrance is blocked even at low grafting level (a), then the grafting spreads to larger pores (<4 nm) (b) and finally a noticeable surface is covered by AQ molecules thus screening the carbon below from the electrolyte and substantially decreasing the double layer capacitance. Reproduced with permission from Reference [142]. Copyright 2011, Elsevier Ltd.

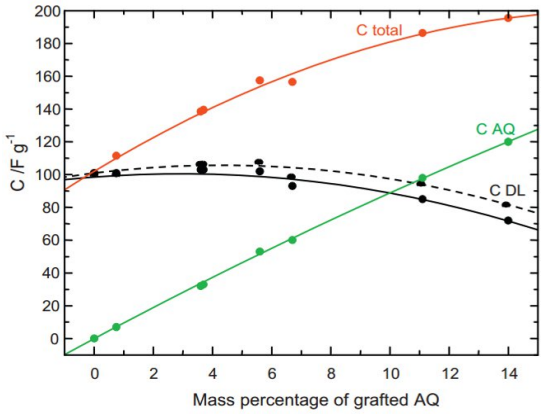

Figure 22 Plot of the total capacitance (C total), AQ capacitance (C AQ) and double layer capacitance (C DL) of the modified carbons as a function of the AQ loading. The dashed curve represents the double layer capacitance relative to the carbon black Pearls content of the modified materials. Reproduced with permission from Reference [114]. Copyright 2011, Elsevier Ltd.

Based on these findings, Lebègue *et al.* [143] investigated the effect of two commercial activated carbons having approximately the same BET surface area but with either a microporous or a mesoporous structure. Results showed that the performance of the microporous carbon was strongly affected by the functionalization while a good compromise between the electrolyte accessibility and the ionic transport was found for the mesoporous carbon which therefore appeared well-suited for the functionalization. Cougnon *et al.* [144] further showed using electrochemical impedance measurements that the functionalization of an activated carbon resulted in an increase of the ionic resistance, making longer the time needed to reach the maximum charge stored more likely due to a lower accessibility of the electrolyte inside the porosity. Note that the authors concluded that in this specific study, the carbon functionalized with redox molecules appeared not suitable for high cycling rate applications compared to the unmodified carbon. Further fundamental studies and new strategies are therefore required to functionalize carbon without affecting the pore structure. In that direction, Cougnon *et al.* [113] proposed a one pot procedure using an initial -NO_2 bearing molecule that was electrochemically reduced to -NH_2 in the vicinity of a glassy carbon surface before to be rapidly covalently functionalized via diazotization. This approach therefore differs from the classical formation of a diazonium salt that starts with a -NH_2 group. Detailed compilation of various coupling strategies for the carbon functionalization is well reviewed elsewhere [25].

As a summary, Table 1 gathers for each purposes discussed in the present review, the functional molecules as function of the substrates and the corresponding chemical reactions / interactions.

5. Conclusions and perspectives

As shown, molecular functionalization has various growing interests in regards to electrochemical storage limitations. According to the targeted applications and required properties, it has been proved that the main merits of the molecular functionalization are the efficiency and versatility of both covalent and non-covalent approaches and more importantly the ability to carefully tune the material surface properties while retaining those of the bulk material. As a whole, whatever the molecular functionalization approach is, monolayer coverage are generally obtained except for the diazonium chemistry for which strict experimental conditions have to be used if one wants to avoid multilayer formation. This aspect is important when porous materials are functionalized as it may decrease electrolyte accessibility in the porous network. Also, if the charge transfer and electronic conductivity are of major concerns when functionalizing carbon substrates, diazonium chemistry may not be appropriate as it forms sp^3 defects. In that case, non-covalent functionalization through π-π interactions should be preferred. Also, further improvements are continuously being investigated.

Based on the present literature report, the following perspectives can be proposed. As a general perspective, it is worth mentioning that in principle, any other electrodes materials than carbons and oxides, such as metal oxides and metal/alloys could also be treated by surface molecular functionalization to improve their electrochemical performances. However, the actual limiting factor for a practical application of molecular functionalization

remains the additional functionalization step(s) required unless *in situ* functionalization can be performed.

Table 1 Functional molecules as function of the substrates and purpose and the corresponding chemical reactions / interactions.

Purpose	Substrate	Starting functional molecule	Chemical reaction / Type of bond	Ref
Artificial interphases batteries	natural graphite	4-nitroaniline	diazotation / covalent	[46]
	graphite	p-carboxylic benzene diazonium salt	diazotation / covalent	[47]
	nano-Si	carboxymethyl cellulose	esterification / covalent	[54]
	nano-Si	4-aminobenzoic acid	diazotation / covalent	[55]
	nano-Si	3-aminopropyltriethoxysilane	silanization / covalent	[56]
	nano-Si	thiophene derivatives	electrochemical / non covalent	[57]
	nano-Si	4-phenylenediamine	diazotation / covalent	[58]
	lithium metal	chlorosilane derivatives	silanization / covalent	[60-62]
	nano-$Li_{1.1}V_3O_8$	4-nitrophenyl diazonium salt	diazotation / covalent	[63]
	nano-$Li_{1.1}V_3O_8$	phenyl phosphonic acid	condensation / covalent	[65]
Molecular wiring batteries	$LiFePO_4$	phosphonic acid derivative	condensation / covalent	[70]
	$LiFePO_4$/MWCNT, $Li_4Ti_5O_{12}$/MWCNT	pyrene derivatives phosphonic acid	LFP, LTO (condensation / covalent) MWCNT (π-π / non covalent)	[75]
	nano-Si/graphite, nano-Si/CNT, nano-Si/graphene	4-phenylenediamine	diazotation / covalent	[76-78]
capacitors	MnO_2/carbon black (Pureblack)	4-phenylenediamine	diazotation / covalent	[126]
Redox batteries	$LiFePO_4$-C, carbons (Csp, C65)	4-nitrobenzene diazonium salt	diazotation / covalent	[80]
	carbon black (C65)	1-nitropyrene	π-π / non covalent	[80]
	carbon nanotubes	pyrene derivative	π-π / non covalent	[84]
	nano-SiO_2	quinone derivative of calix[4]arene	condensation / covalent	[87]
	carbon black	4-aminobenzoic acid	diazotation / covalent	[87, 88]
	carbon black-COOH	quinone derivative of calix[4]arene	condensation / covalent	[87, 88]
capacitors	carbon black (Printex XE2)	2-nitro-1-naphthol	adsorption / non covalent	[108]
	carbon fabric (Spectracarb 2225)	anthraquinone-1-diazonium chloride	diazotation / covalent	[109-111]
	carbon fabric (Spectracarb 2225)	4-aminocatechol	diazotation / covalent	[111]
	activated carbon	N-(2-aminoethyl)-1,8-naphthalimide, 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl	diazotation / covalent	[112]
	glassy, activated (Black Pearls) carbons	1-aminoanthraquinone, 2-aminoanthraquinone	diazotation / covalent	[114, 115]
	glassy, activated carbons	2-amino-9,10-phenanthrenequinone	diazotation / covalent	[117-119]
	glassy, activated (Norit) carbons	2,3-dihydroxy-7-nitrophenazine-1,4-quinone	reduction + diazotation / covalent	[120]
	polystyrene, activated carbons	3,4-dimethoxyphenyldiazonium salt	diazotation / covalent	[121]
	carbon fibers	pyrene derivative	π-π / non covalent	[31]
	oxygen-functionalized FWNT	pyrene, 1-amino-pyrene, 1-pyrenecarboxylic acid	π-π / non covalent	[122]
	activated carbon	1,10-phenanthroline	π-π / non covalent	[123]
	graphene	Anthraquinone	π-π / non covalent	[124]
	graphene aerogel	Alizarin	π-π / non covalent	[125]
Wettability batteries	$LiFePO_4$-C	4-amino-benzene-trifluoromethylsulfonimide	diazotation / covalent	[102]
	$LiFePO_4$-C	4-bromoaniline, 4-phenylenediamine	diazotation / covalent	[83]
	ordered mesoporous carbon	4-phenylenediamine	diazotation / covalent	[105]
capacitors	carbon black	4-Aminobenzenesulfonic acid	diazotation / covalent	[127]

Molecular functionalization appeared promising for the formation of an artificial SEI and should receive more attention especially for high voltage application as it should allow great improvements if coupled to the electrolyte additive approach. In that direction, the material surface modification can be used as starting/anchor point for further functionalization. For instance, the covalent anchoring of polymer electrolyte or any other solid electrolyte to the active material surface should in principle lead to both a better wettability and interfacial stability.

Considering the wiring approach, coupling the active material and/or carbon additive to the current collector could be used to solve the impedance and mechanical issues related to the current collector/electrode interfaces encountered in current Li-ion batteries.

While redox functionalization has been clearly proved to be promising for both batteries and electrochemical capacitors, the main limitation remains the limited number of electrons exchanged per molecule. The design of new organic multi redox molecules coupled with cheap and eco-friendly synthesis processes is highly sought after. The use of redox polymer that would be anchored to the active material substrate and would replace both the binder and the conductive carbon additive is also a promising approach.

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